

“Opportunities for the Dynamical Investigation of Primary Processes in Radiation- Physics, Chemistry, and Biology”

Proposed Experiments:

Fs X-Ray-Pump / Visible-Probe

Fs X-Ray-Pump / X-Ray-Probe

What is the structure and dynamics of the conduction band?

BACKGROUND

**IONIZING RADIATION IN WATER AND
AQUEOUS SOLUTIONS PRODUCES IN ~ 700
FS:**

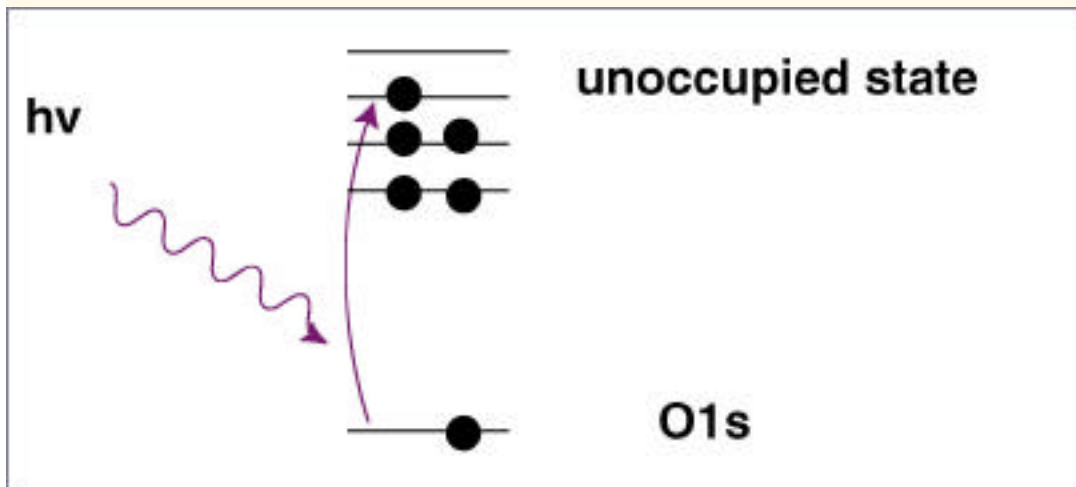
- **Hydrated electrons**
- **Hydroxy radicals OH**
- **H₂**
- **H₃O⁺**

**THESE SPECIES, ESPECIALLY THE OH RADICALS,
DAMAGE DNA AND OTHER BIOMOLECULES
LEADING TO THE MEDICAL CONSEQUENCES ON
IONIZING RADIATION:**

1. RADIATION TREATMENT

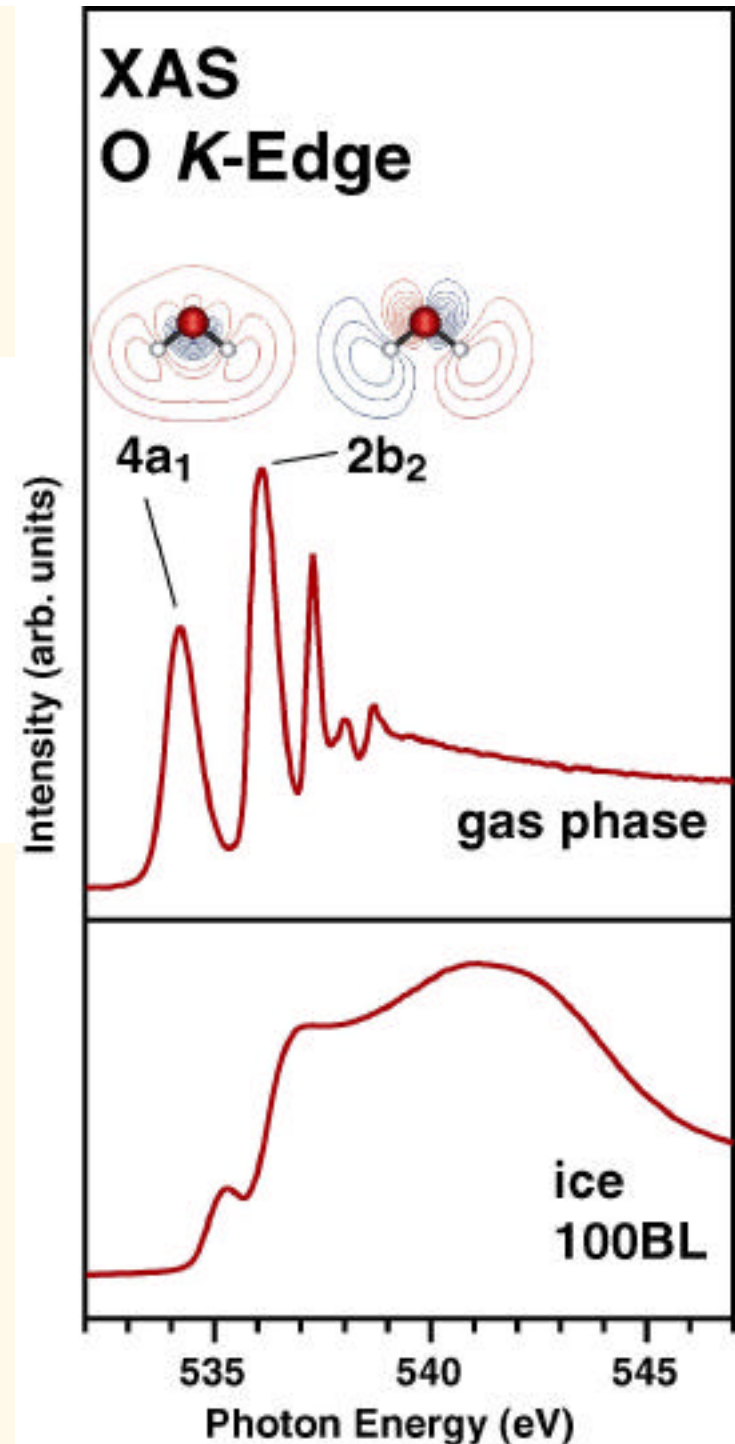
2. RADIATION INDUCED MUTATIONS

X-ray Absorption Water



Initial absorption event is followed by cascade of many e/hole pairs (< 20)

A. Nilsson
(SSRL)



THE ENERGY DEPOSITED BY THE IONIZING RADIATION INVOLVES MULTIPLE-CASCADE PROCESSES IN THE FIRST 100-200 FS THAT HAVE NEVER BEEN TIME RESOLVED, INCLUDING:

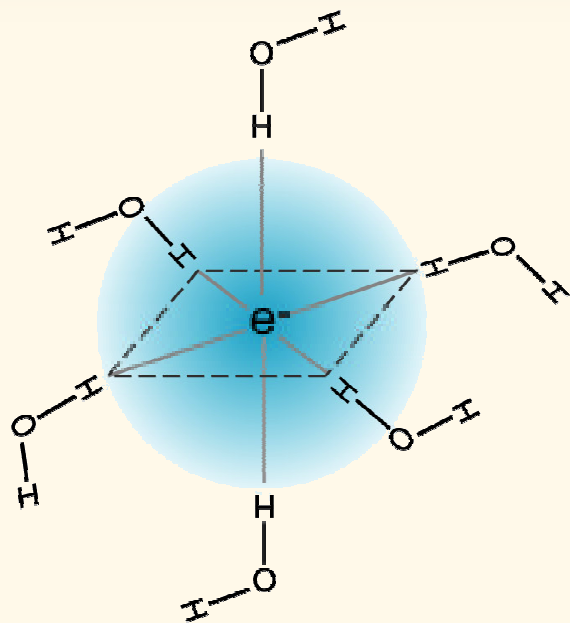
Conduction band population, depopulation and relaxation

Secondary electron generation

Excited State Dynamics

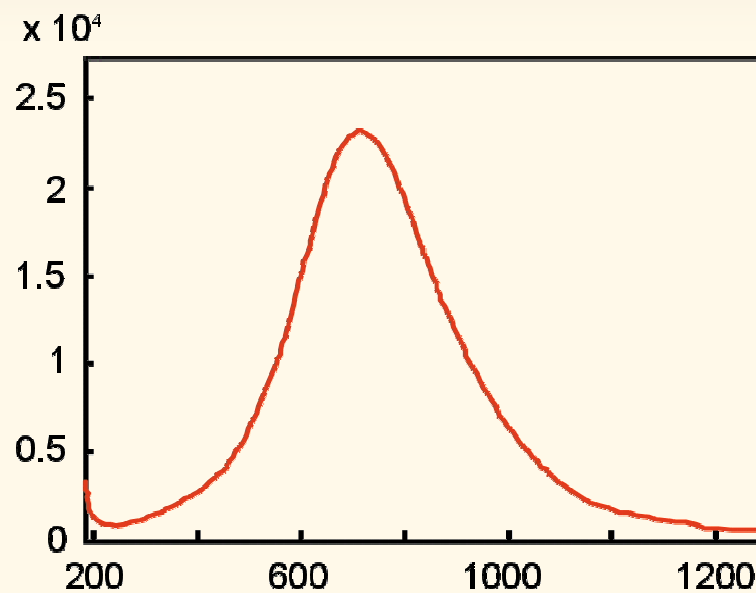
Solvated Electron Trapping and relaxation

Background - Structure and Spectroscopy



**Structure of the
ground state**

Absorption spectrum



Nanometers

Spatial Extent and Reactivity Conduction Band Electrons in Water

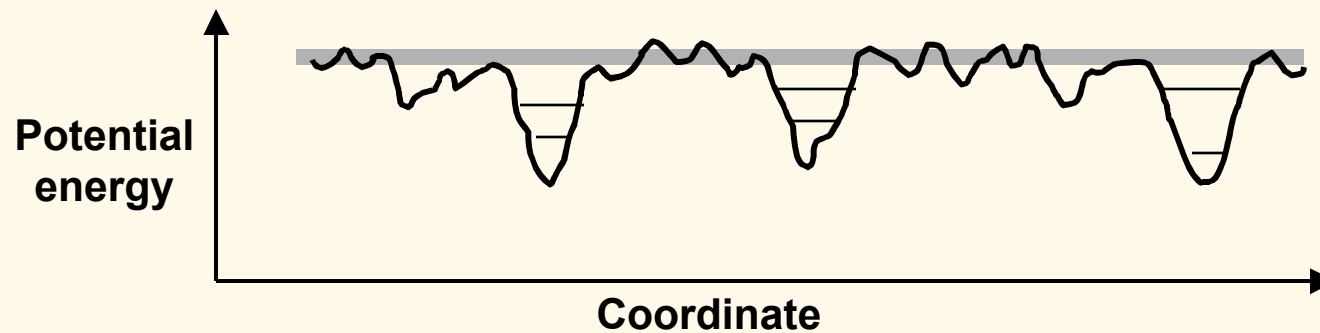
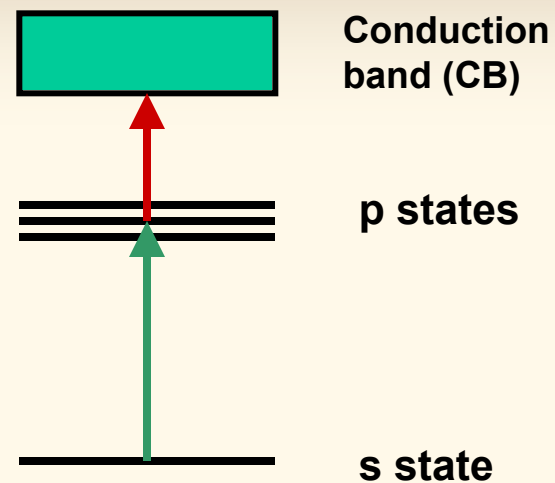
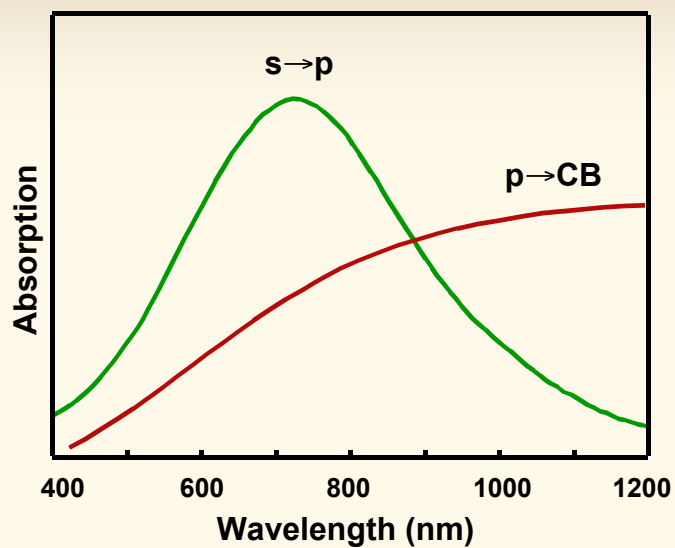
Dong Hee Son, Tak Kee, and Paul Barbara
Department of Chemistry and Biochemistry
The University of Texas

- **Hydrated electron** is a simple and fundamental species in solution phase chemistry
- **Excited States of the Hydrated Electron** offer insight on the nature of conduction band like states in liquids
- **Highly Relevant to Radiation Chemistry and Physics** (including Ultrafast X-ray Experiments)

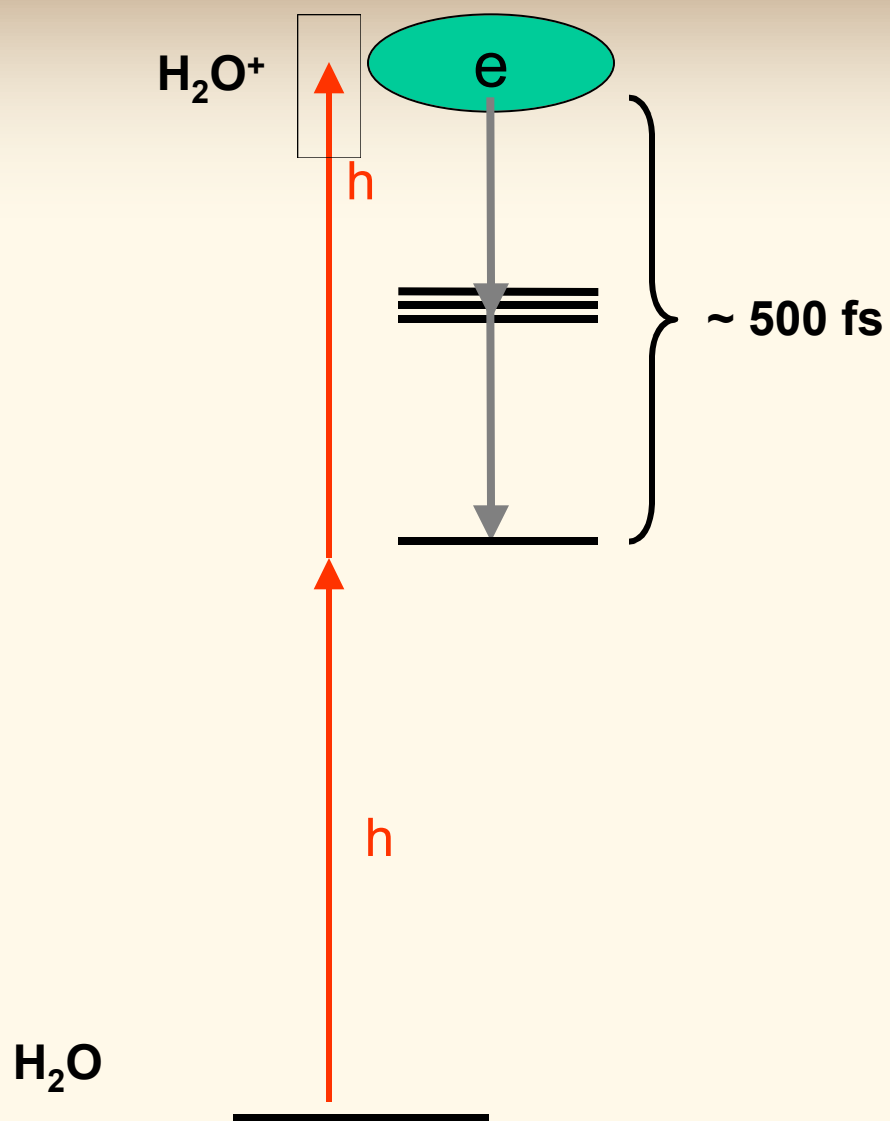
Hydrated electron

- Structure
 - Chemistry
 - Relaxation Dynamics
- } of the excited states

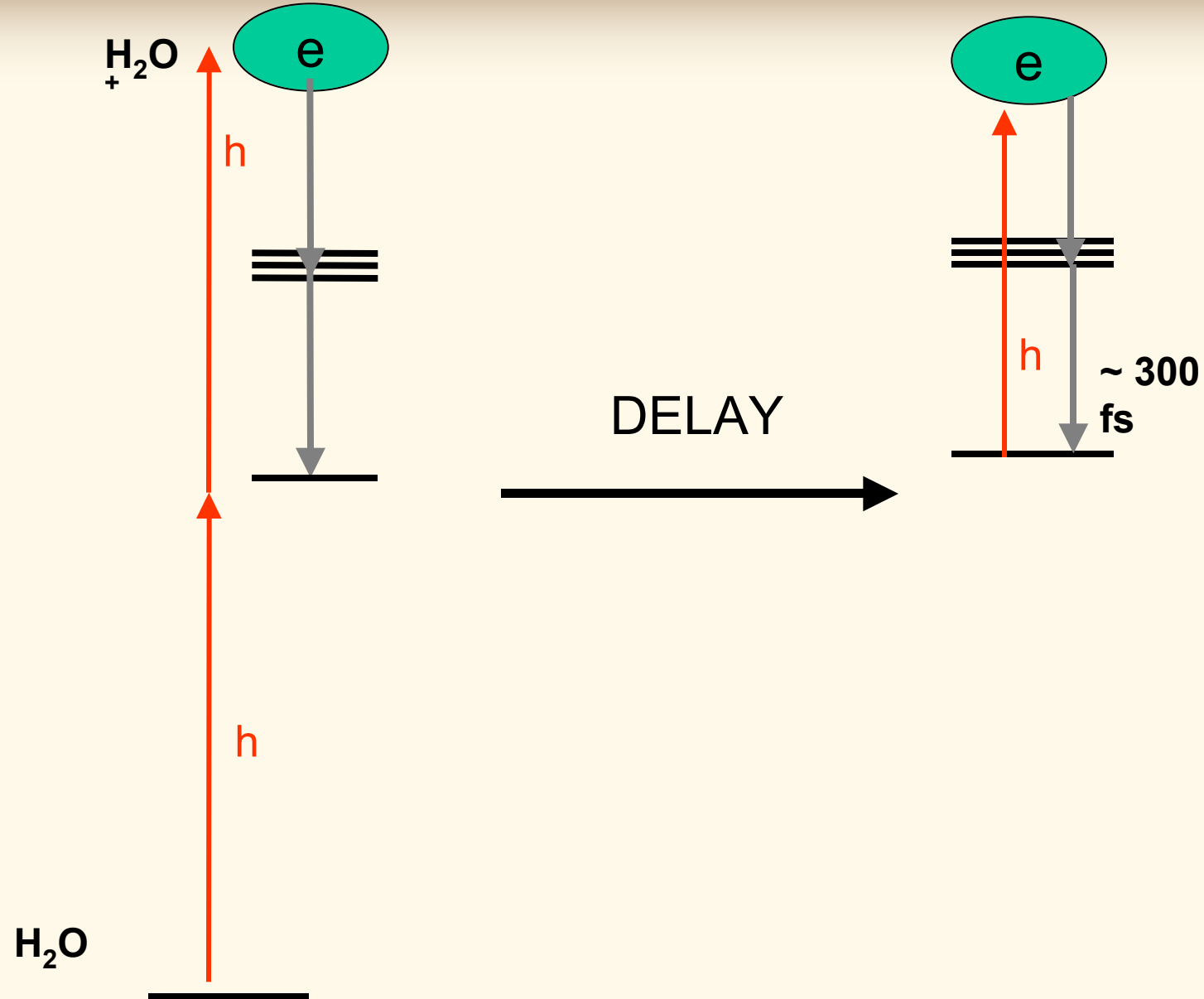
Background - Structure and Spectroscopy



Multi-Photoionization/Probe

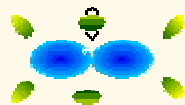
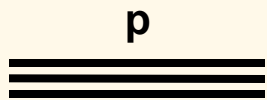


Multi-Photoionization/Pump/Probe



Structure (Size) of the Hydrated Electron

CB



s



Theoretical

Experimental

N/A

✓ This study

$$\langle r \rangle_{pl} \approx 2 \langle r \rangle_s$$

✓ This study

$$\langle r \rangle_s = 2.7 \text{ Å}$$

3 Å

Measurement of the Spatial Extent of p, CB Electron

Photo-induced suppression of geminate recombination

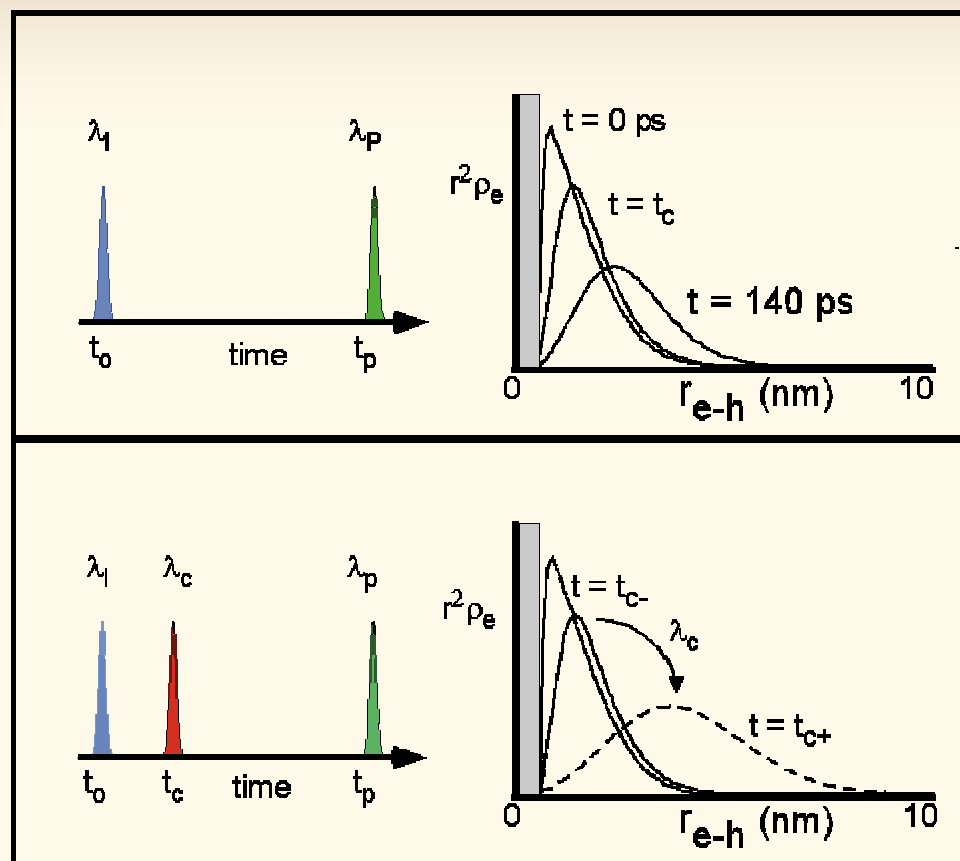
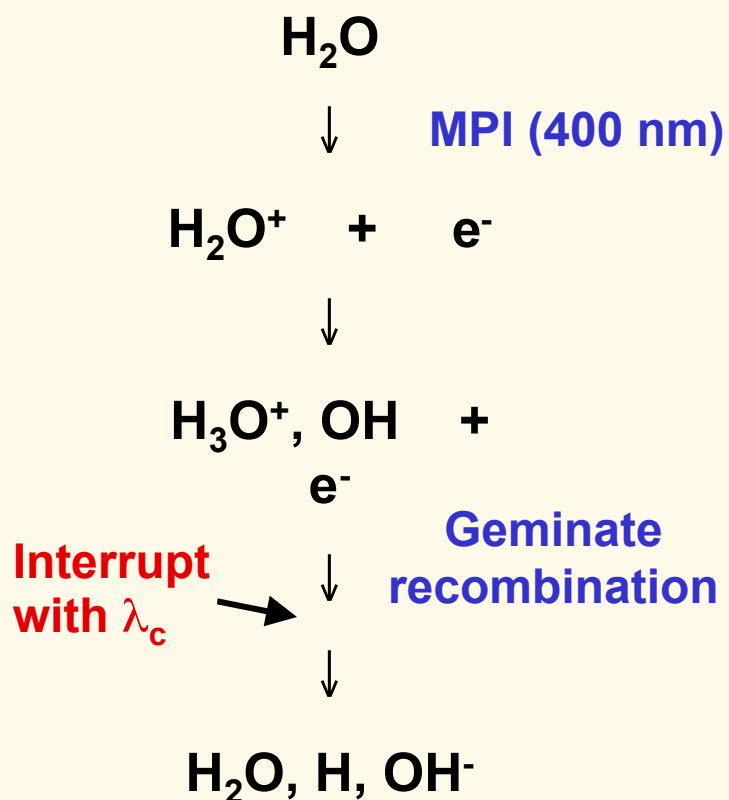
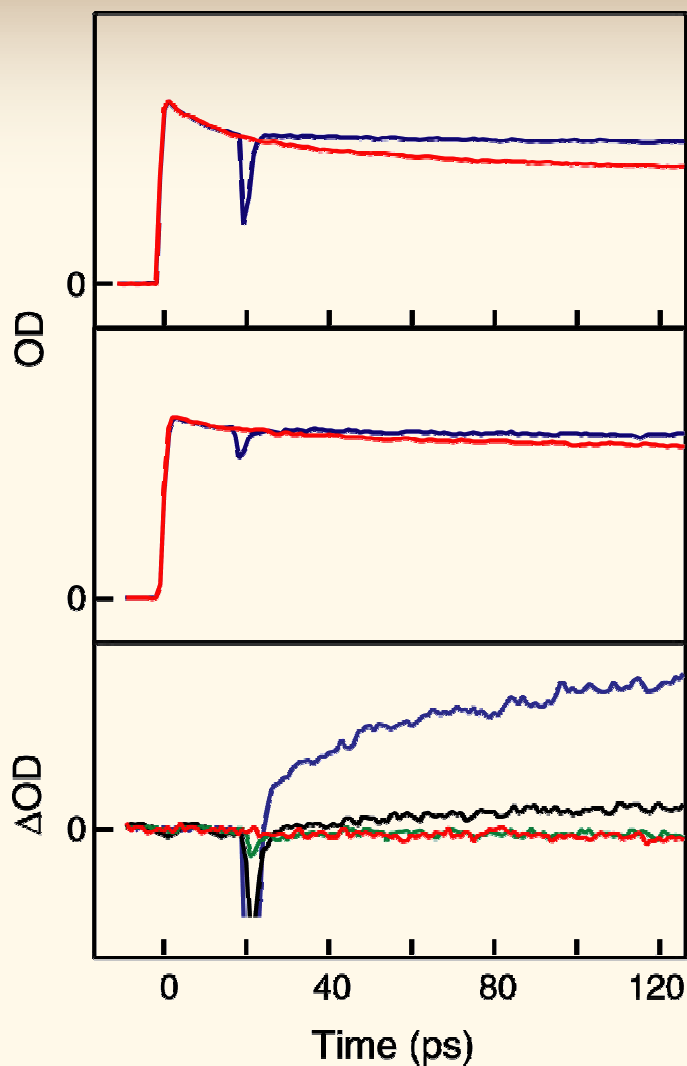


Photo-suppression of Geminate Recombination (GR)



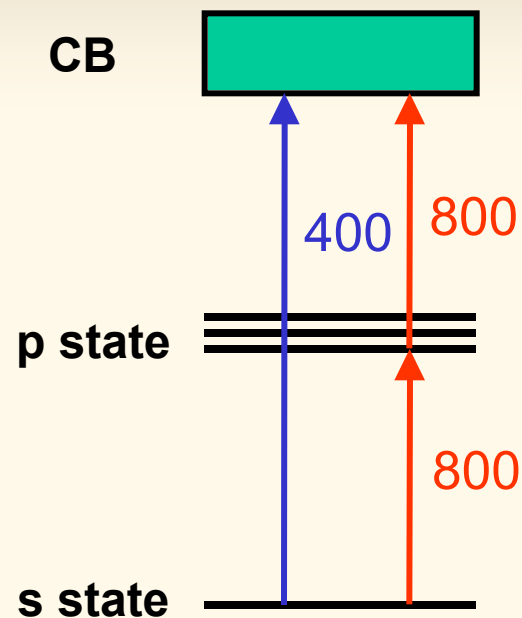
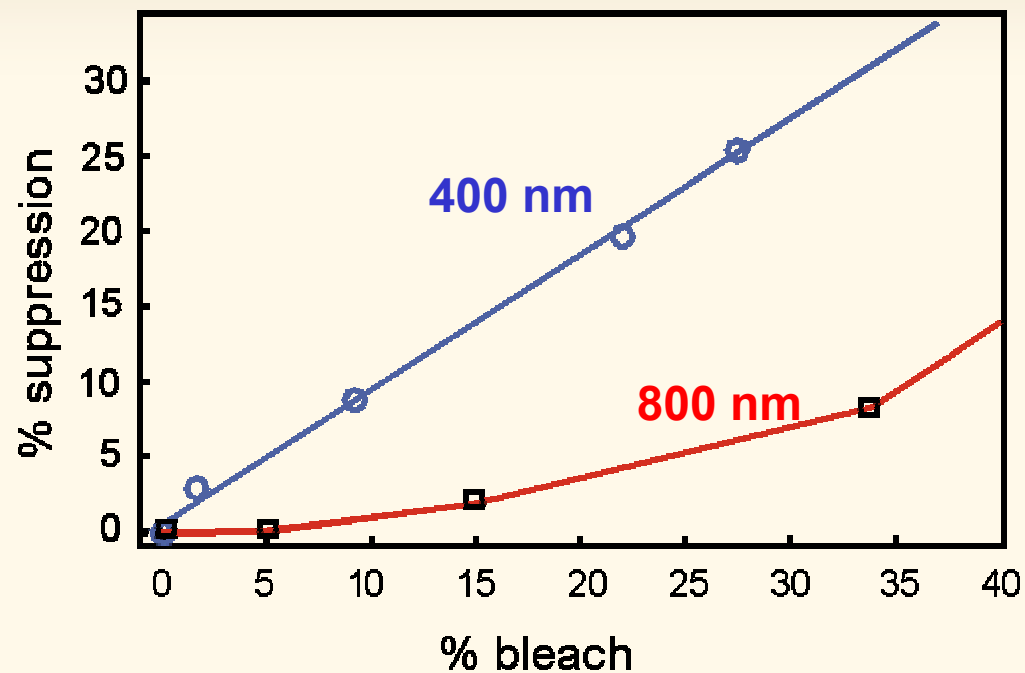
Ionization pulse : 400 nm (or 266 nm)

Suppression pulse : 800 nm

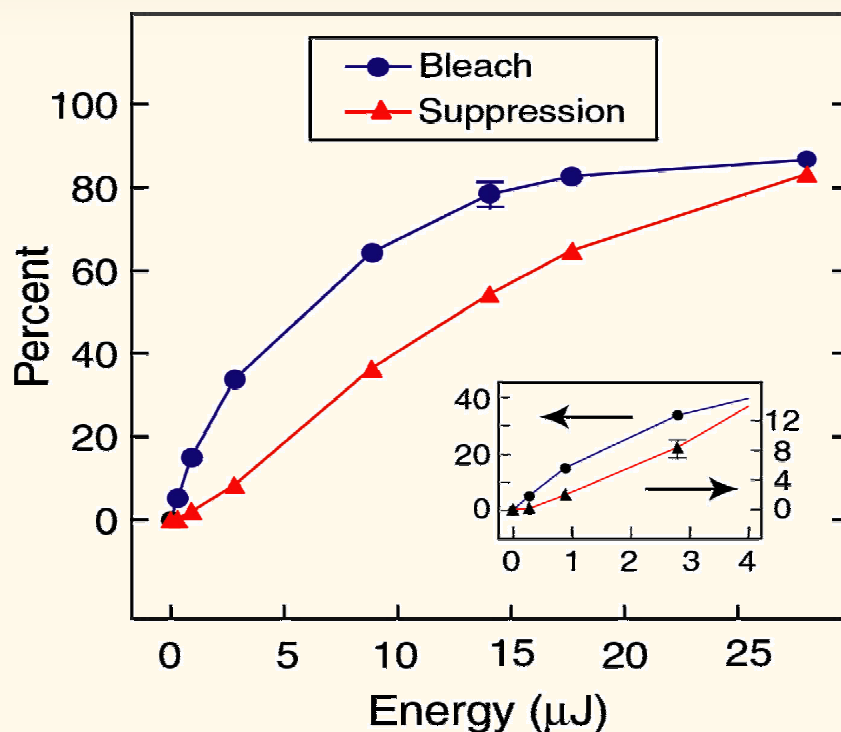
Probe pulse : 650 nm

- **Geminate recombination kinetics is strongly suppressed due to excitation of the hydrated electron by the suppression pulse at 800 nm**

1-photon vs. 2-photon Route to Conduction Band



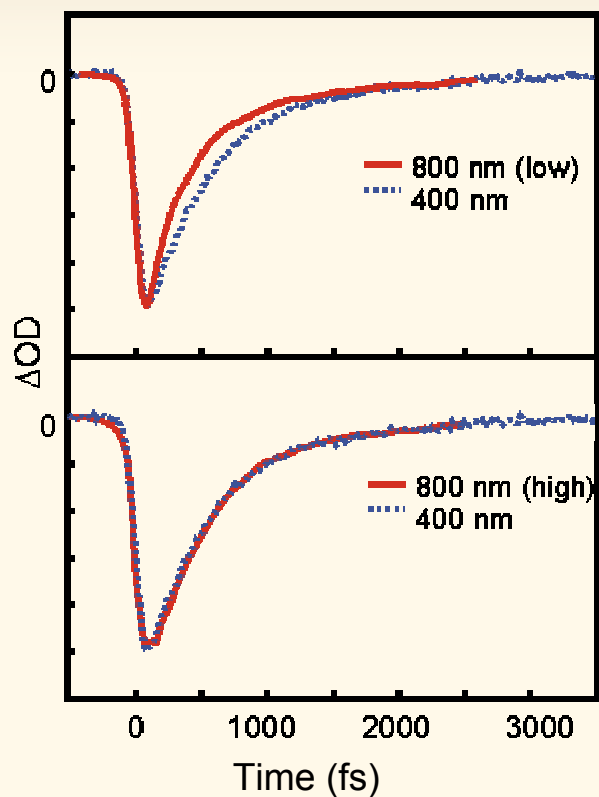
Suppression Pulse Energy vs. % Suppression of GR



At low suppression pulse energy;
Bleach is *linear*,
Suppression is *quadratic* to the pulse energy at 800 nm

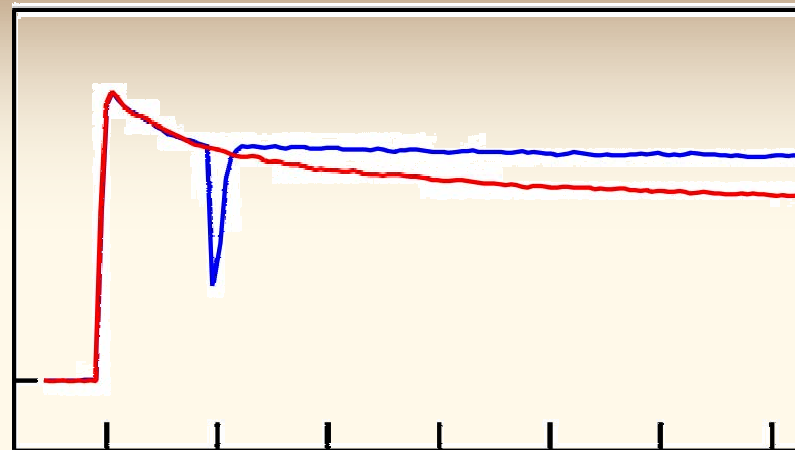
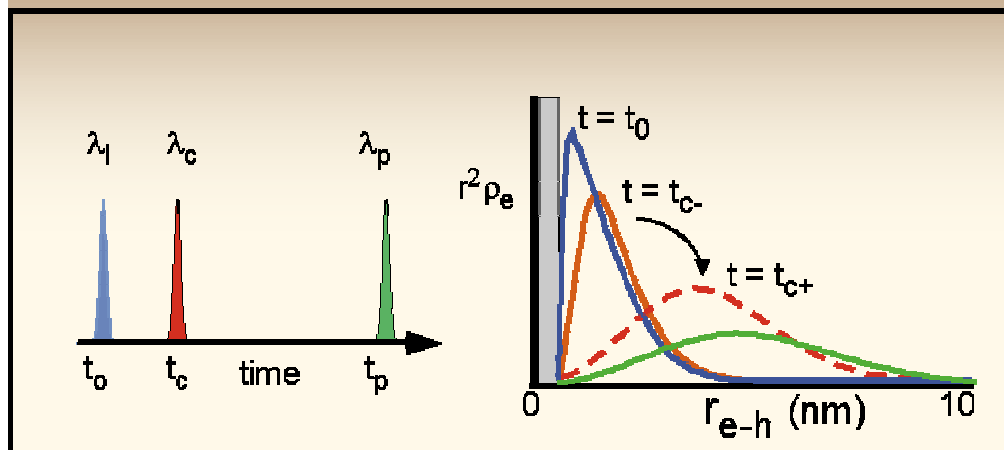
Suppression correlates with two photon process - only CB electron is responsible for suppression

Comparison of 1-photon and 2-photon CB State



- Excited states reached by excitation with weak 400 nm and strong 800 nm exhibits identical electronic relaxation dynamics
- Both states are identical CB state

Modeling of the Photo-suppression of GR



Initial e^- distribution



Calculate $e^-(r,t)$,



Estimate a migration length and calculate $e^-(r,t)$ at $t=t_{c+}$ at a given λ_c energy



Compare with data



Calculate $e^-(r,t)$, $S(t)$ for $t > t_{c+}$



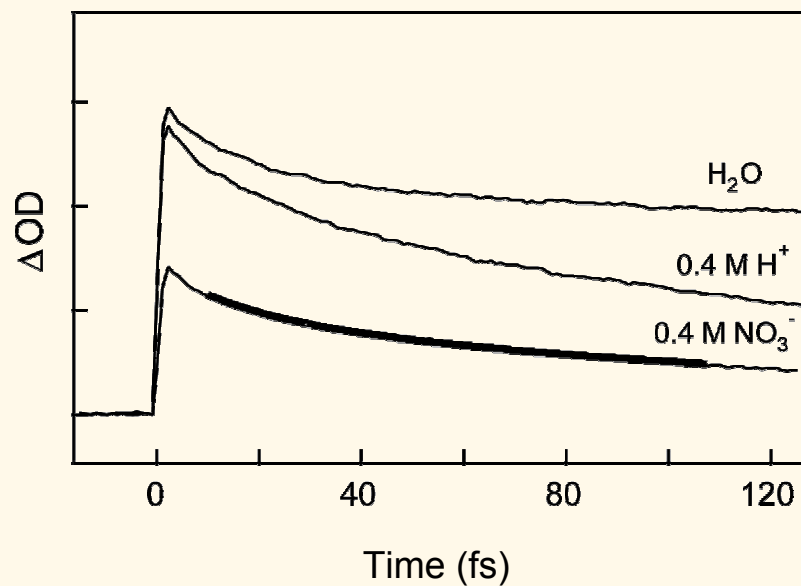
Migration length

CB $> 30 \text{ \AA}$

p $< 3 \text{ \AA}$

Scavenging Reaction of the Hydrated Electron

Hydrated electron is a strong reducing agent



Reactions involving e^-

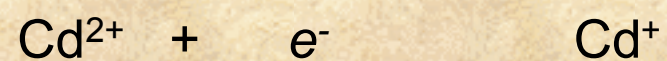
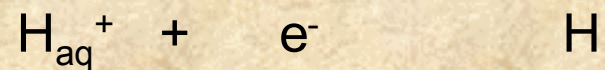


Photo-induced Scavenging of the Hydrated Electron



photo-induced
scavenging

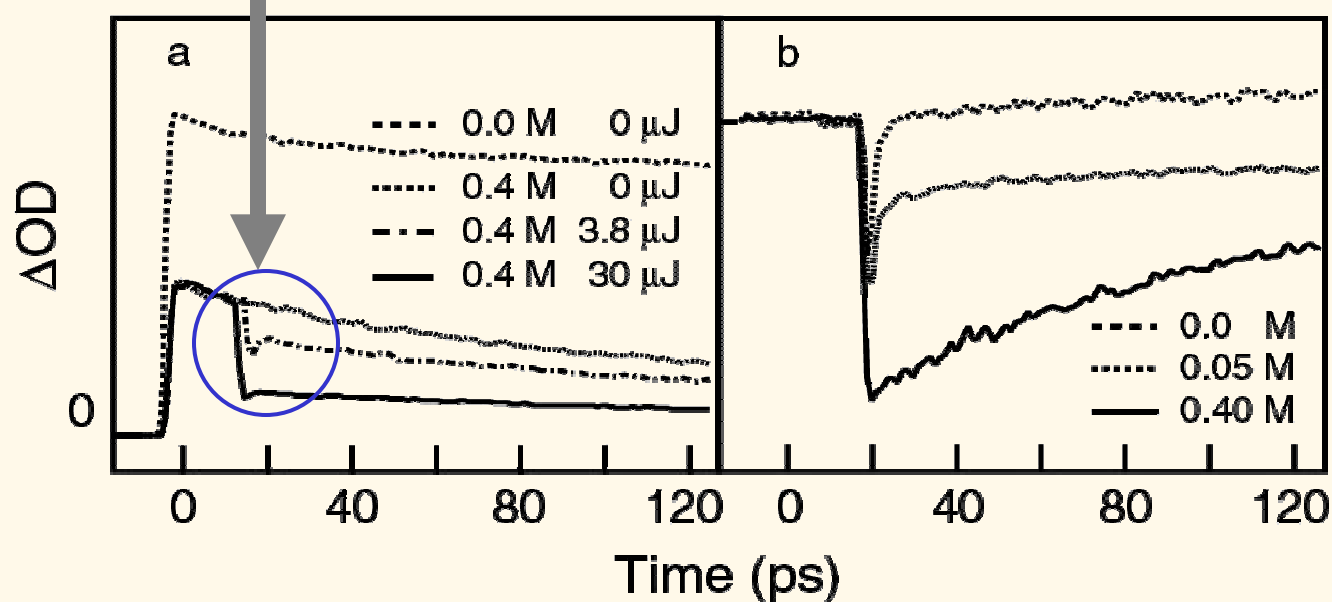
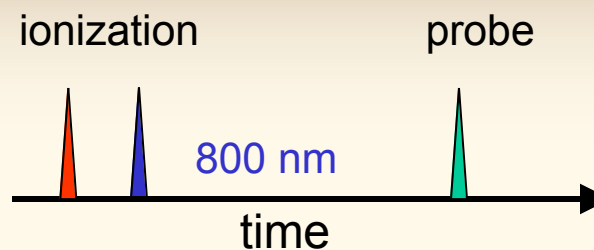


Photo-induced scavenging is static scavenging !

Photo-induced Scavenging Yield vs. Pulse Energy

